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# Migration of elements in colour layers deposited on a ceramic substrate under the influence of laser treatment

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**Abstract**

This paper summarizes the experimental results in the laser firing of colour agents on ceramic substrates. White glazed and fired ceramic plates were used as the substrate, while the deposited powders were mixtures containing ceramic colours and other colour agents. Various geometric patterns were deposited by a cw fiber Yb:YAG laser with speed controlled by a set of galvanometric scanners. The results, analyzed by means of optical microscopy, SEM EDS and laser profilometry explained the visually observed changes in pattern colours caused by the migration of pigment particles (characteristic elements) and allowed development of proper laser process.



*Keywords:* ceramic colour; enamel; laser marking

## 1. Introduction

Laser radiation is an ideal tool for industrial processing as it does not introduce any admixtures that might change the chemical composition of the material. The radiation laser energy may be applied to a specifically determined place, in the desired time and quantity. The work may be restricted to the exact selected area, without the need for masking off its surroundings. The surface of areas that are difficult to access or have a large curvature may be processed. Special optical mirror systems allow the processing of parts that are not directly visible. It is a non contact method so it allows for the processing of hot, toxic or radioactive materials.

Amongst the various laser processing methods available, one of the most popular uses is for marking. In principle all types of industrial lasers are used for this, and the list of materials that can be marked is practically unlimited and includes materials such as: metals, plastics, ceramics, glass, wood, leather, paintings, photographs,

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paper and many others [1-3]. The ceramics industry is also interested in the use of lasers for the execution of tasks such as for example marking, printing, labelling, glazing and powder sintering. Traditional methods for decorating ceramics utilize designs that are first painted with ceramic colorants onto the surface of the product. These are then fired in a high temperature furnace so as to achieve a smooth surface of the decoration and assure adhesion to the surface it was applied to. Instead of heating a whole batch in a furnace, a focused laser beam exclusively heats up the printed area without affecting the rest of the product in a process that saves time and energy.

The work presented in this article was completed in The Institute of Ceramics and Building Materials in Warsaw. The purpose of the work was elaboration of a process for achieving coloured print using sintered decorative agents onto the surface of ceramic products.

## 2. Overview

The firing of ceramic colour agents on typical ceramic substrates requires many preparatory processes, specifically:

- Development of a colouring agent suitable for laser processing and also suitable for the given substrate;
- Preparation of the substrate (for example washing);
- Preparation of the decorative suspension or paste;
- Application of the suspension/paste onto the ceramic surface;
- Drying;
- Laser firing, sintering of the decorative agent with the substrate.

Each of the above mentioned processes has a great influence on the final fired result [4-8]. Due to a lack of place these operations will not be described here since they are specific to the individual colouring agents and ceramic substrates.

The laser treatment should satisfy a number of requirements that are conditional for its usefulness in the practical process of decorating ceramics:

- The decorating agent should be permanently bonded with the substrate as a result of laser irradiation;
- The marking should produce the desired colour from the decorative agent used;
- The surface of the marked area should be smooth and lustrous.

The simultaneous fulfilment of all of these criteria is a difficult process task and also difficult due to the required optimization of the laser parameters.

For all of the samples presented, a Yb:YAG continuous wave fiber laser model SP-100C-0016 from SPI Lasers, UK with a maximum power of 100 W working with a wavelength of 1090 nm was used. The laser beam was focused on a selected point on the work surface by a Raylase RLA-1004/Y/D2 galvanometer scanner equipped with a F-theta lens with a focal length of 160 mm. The laser beam was controlled by weldMARK™ software. A number of sets of working parameters were defined for the weldMARK™software, which allowed the optimal irradiation parameters to be identified for the individual colorants.

## 3. Results of the profilometry studies

The optical profilometry technique is a standard method for grading the condition of a surface that reflects light. This method can be used to determine the roughness and structural unevenness that has come about as a result of various processes to which an object has been subjected. A Veeco NT9300 optical profiler was used in the studies to determine the line profile and parameters $R_a$ and $R_z$.

In the studies, ceramic samples were covered with a test black decorating agent, containing Co, Cr, Ni and Fe compounds, operationally named MS-14. Measurement of the line profiles were conducted for a number of different laser beam powers. This allowed for the effects of the surface tension forces and also the plasma recoil pressure to be seen in the line profile (Figs 1 and 2). According to the discussion presented in [8], it may be assumed that the possible driving forces of the observed profiles are surface tension gradients in the melt (the Marangoni effect) and the laser plume recoil pressure due to evaporation. Surface tension in the presented case was not investigated.

However, according to the theory described elsewhere [8,9], surface tension forces depend on the temperature of molten material (thermocapillary effect), or the content of surfactants (chemicapillary effect). In any case, the pigment material underwent melting and evaporation under the action of a laser beam. In the molten material surface tension forces generally decrease with increasing temperature, causing in the present case undesired depression in line profile. Atmospheric gases dissolved in the molten materials may act as surfactants and they may increase surface tension forces in some cases. The result of chemicapillary effect related to such surfactants is the tendency to the formation of bulges due to movement of the liquid phase from a region with a low value to a region with a high value of surface tension forces [8].

Figure 1 shows the line profile for the sample illuminated by a low power 7.5 W laser beam, and Fig. 2 shows the line profile for a power of 17.5 W. The scanning speed in both cases is 15 mm/s. When the laser beam has a low power the plasma recoil pressure is also low and the shape of the line profile is in this case determined principally by the surface tension forces (Fig.1). The elevation in the centre of the line may be related to the chemicapillary effect. When the power of the laser is increased, the plasma recoil pressure in the centre of the line also increases. As a result of the interaction between the plasma recoil pressure and the surface tension forces, a line profile with a depression in the centre is attained (Fig.2). The role of the plasma recoil pressure and the surface tension forces in shaping the line profile are presented in detail in [8].

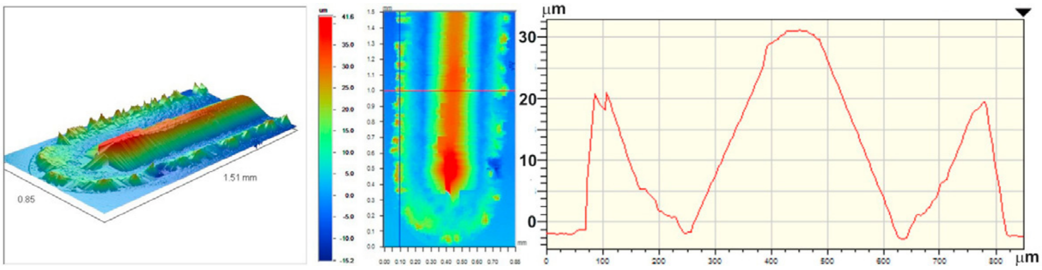



Fig. 1. Results of the line profile studies for the fused MS-14 decorating agent, illuminated by a 7.5 W fiber laser beam with a scanning speed of 15mm/s. Shown on the left are the gradient images for the studied line area. Shown on the right side is the line profile for the place indicated by the line in the image on the left. $R_a = 8.3$ µm, $R_z = 51.5$ µm

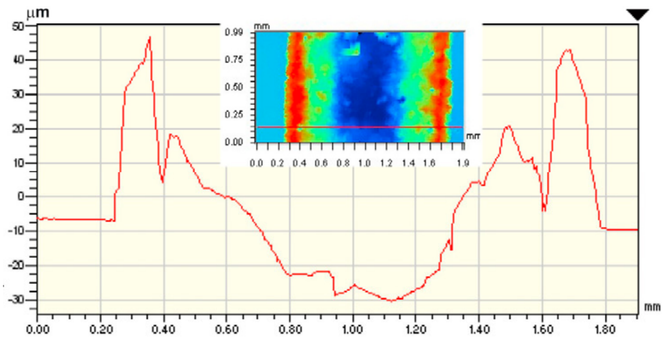



Fig. 2. Results of the line profile studies of the fused MS-14 decorating agent, illuminated by a 17.5 W fiber laser beam with a scanning speed of 15mm/s. Gradient image for the studied line area is shown in the upper-central part of characteristic

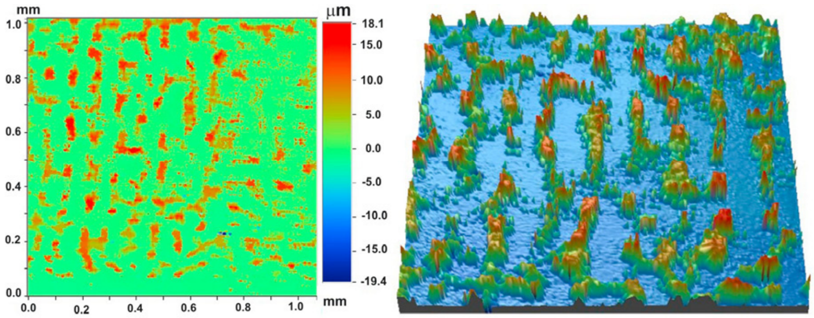



Fig. 3. Profilometric imaging of squares covered in 1NK1/M commercial blue onglaze ceramic colour [10], illuminated by a 100W laser with a scanning speed of 1250 mm/s. $R_a$ = 2.9 µm, $R_z$ = 26.6 µm

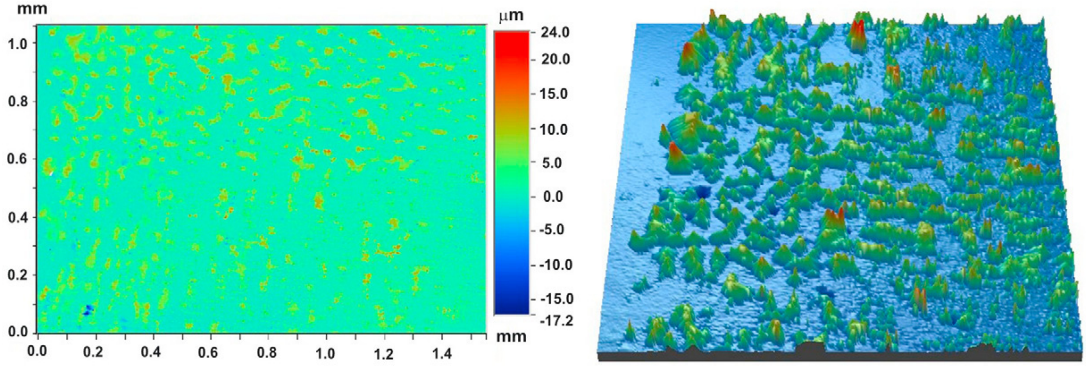



Fig. 4. Imaging of the profile measurement of squares covered in commercial blue onglaze ceramic colour 1NK1/M [10], illuminated by a 100 W laser with a scanning speed of 1250mm/s. $R_a$ = 1.9 µm, $R_z$ = 25.1 µm

Fig.3 and Fig.4 display the results of surface sintering 1NK1/M commercial blue onglaze ceramic colour [10] containing Co as the colorant on a white ceramic substrate. The laser beam power was 100 W and the scanning speed was set to 1250 mm/s. The effects of filling in the square area on the sintering were assessed. Results of the illuminations on the squares turned out to be dependent on the power of the laser beam, the scanning speed, the laser absorption coefficient and the coefficient of conductivity of the materials subjected to the process. The scanning speed and laser power determine the effect that these two factors have in forming the structure of the sintered layer and depending on their values the effect on sintering was different. Fig.3 displayed the results of sintering a square sample using parallel lines spaced at a distance of 0.1 mm from each other. The square was illuminated once. A linear relief can be observed on the glazed structure in the scanning direction of the laser beam. Fig.4 displayed the results from when the square sample was illuminated second time by rotated (90°) parallel lines spaced again at a distance of 0.1 mm from each other, so finally the square was illuminated twice. Parameter $R_a$ has a value of 2.9 µm in the first case and 1.9 µm in the second. It is possible to see that in the case of the sample that was illuminated twice the sintered layer is less rough, however the process requires a longer illumination time.

## 4. Results of the studies of the geometry and the chemical composition of the lines

The sintered areas of the samples covered with a 1X-Z3 commercial green onglaze colour [10] containing chrome were analyzed (Fig. 5). Fig. 6 shows photographs of perpendicular cross sections of selected lines 1 and 25 made with the use of a scanning electron microscope. It is important to note the cracks caused by thermoelastic stress and that the track is not bonded to the substrate.

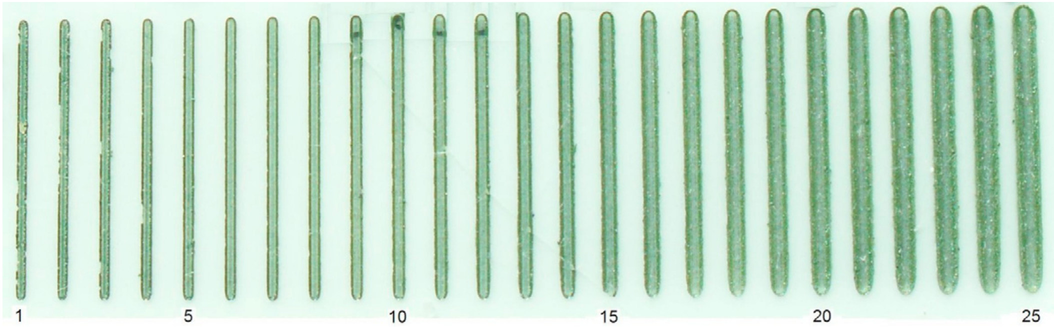
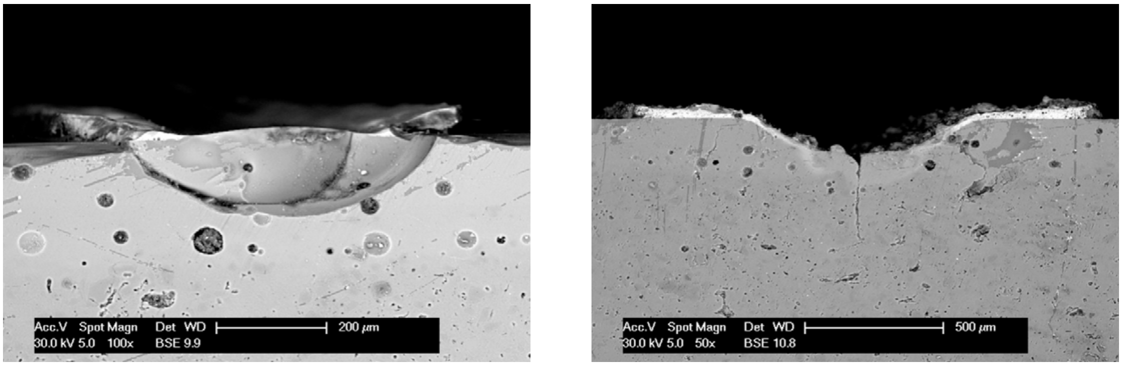



Fig. 5. Photograph of lines of 1X-Z3 commercial onglaze colour [10] illuminated by a 20W laser beam. The length of every line is 20 mm. The scanning speed was changed linearly from 20 mm/s for line 1 to 2 mm/s for line 25, with a step change of 0.75 mm/s between lines




a) b)

Fig. 6 SEM photographs of selected characteristic sample tracks covered with the 1X-Z3 green colour: (a) cross-section of line 1 in Fig.5; (b) cross-section of line 25 in Fig.5

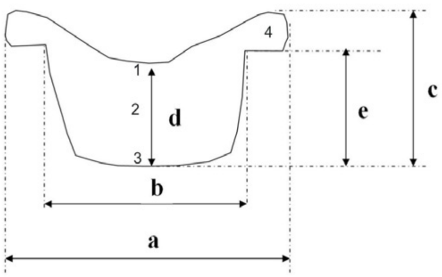



Fig. 7. Shape of the line and definition of the parameters that characterize its geometric dimensions. The numbers 1, 2, 3 and 4 show the points where chemical analysis was performed

The majority of the lines are characterized by the shape shown in Fig. 7. The numbers 1, 2, 3 and 4 in the Fig. 7 indicate the positions of points in which chemical analysis was performed. The figure also shows the marked areas and their dimensions. These have been studied further. The following parameters were selected to characterize the lines: a – total width of the line; b – width of melt; c – total depth; d – depth of the melted zone measured from the bottom of the crater; e – depth of the melted substrate zone from the base surface of the ceramic substrate. The values of these parameters were provided after the analysis of photographs from an electron microscope. Plots of these parameters as a function of the energy density of the laser beam are shown in Fig.8.

In the example presented in Fig.5, chrome is the element that determines the colour. Fig.9 presents the distribution of the concentration of chrome in a cross section of the weld with the substrate of line No. 11 (power 20 W, energy density 325 J/cm$^2$).

The laser treatment causes the transfer of elements within the line. This is associated with the hydrodynamic flow of the melted colour agent and the substrate. During laser treatment, some of the colorants may be chemically degraded and may also evaporate. These undesired phenomena cause a change in the concentration of individual elements, which results in a colour change within the line.

Chrome compounds have almost completely vanished from the fusion zone. These losses are not explained by the small increase in concentration (for larger energies) in area 4 due to the incomparable volume of this area and the complete melted area. It is most likely that Cr has vaporized, and maybe this was even preceded by the breakdown of its compounds due to the temperature generated in the processed area. This is confirmed in the photo (Fig.5), where all of the lines are lighter in the centre, and their colour is closer to the white colour of the substrate. The greenish colour is due to the presence of chrome in the surface layer (area 1). The borders of the lines give the colour of the pigment, and this is confirmed by the results of the measurement of the concentration of area 4 (intensive green). The optimal process must thus be conducted so that the compounds that define the colour of the applied colorant are retained in the fusion zone.

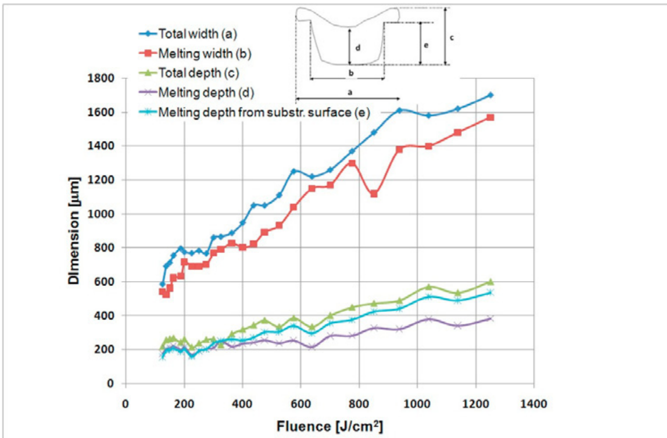
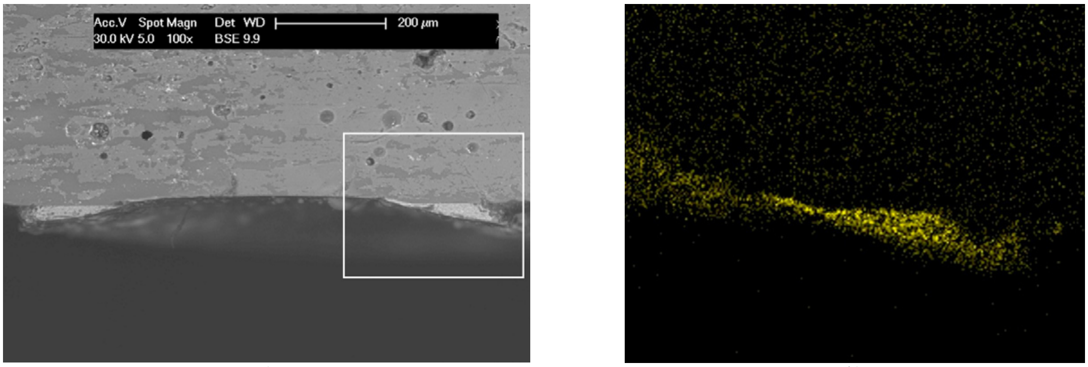



Fig. 8. Graphical representation of geometrical measurements on the melted areas as a function of the laser energy density




a) b)

Fig. 9 Distribution of chrome concentration in the perpendicular cross section of line 11 (Fig.5): (a) SEM photograph in SE mode; (b) Cr distribution inside white square in (a) - the brighter the area the higher Cr content

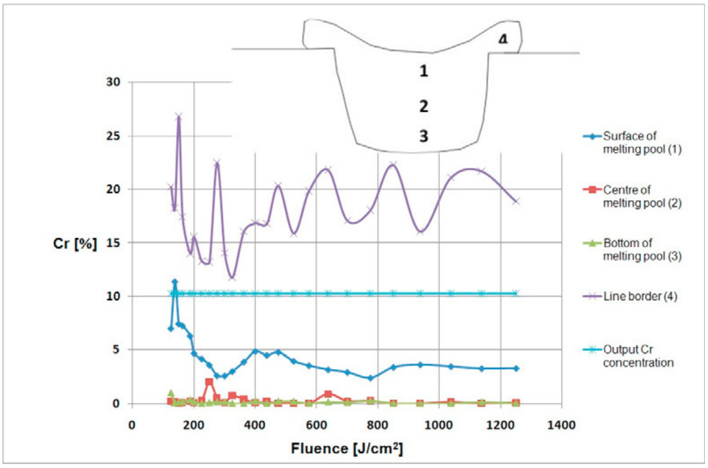



Fig. 10. Distribution of chrome concentration in the individual areas of lines as a function of the laser energy density

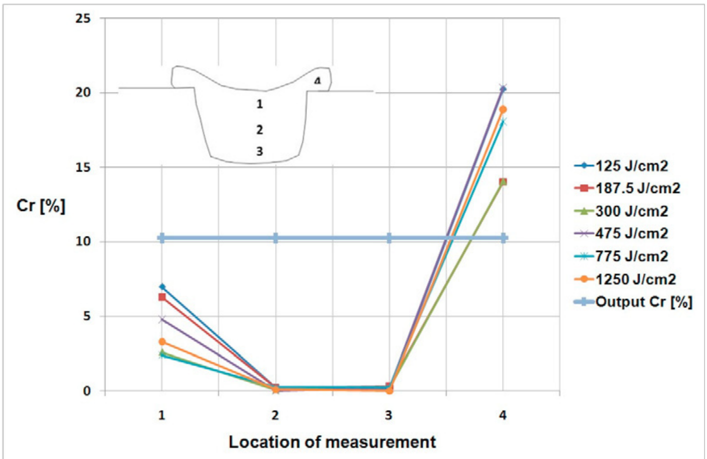
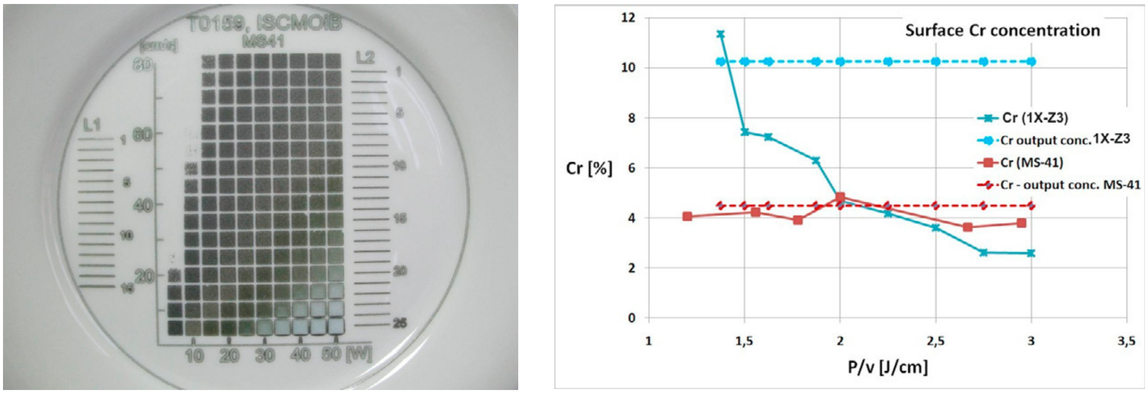



Fig. 11. Changes in the concentration of chrome in different sample areas at different laser energy densities

The fluctuations in content visible in Fig.10 are most likely to have been caused by the measurement method. From the photos in Fig.9 it seems that the colorant after crystallization separates into polycrystalline grains of different compositions, which is why the chrome in the colorant is not deposited in a uniform way but exists as polycrystalline grains, which cause the fluctuations in the measurement results that can be seen in Fig.10. A more precise measurement of the elementary composition would require an averaging after numerous measurements. Additionally, changes in the concentration of chrome in different areas of the melt pool are illustrated in Fig.11. Assuming that the average chrome content in area 4 (at the border of the track) is about 20 %, it can be concluded that the concentration in this area has increased up to twofold in comparison with the starting content of chrome in the colorant. At the same time it has almost completely disappeared from the area where the laser beam has been directly applied.

Fig.12a shows photos of the ceramic plate where the MS-41 test black colour agent has been applied and has been illuminated by a laser with a wide range in the scanning speeds and the laser powers. Chrome is one of the elements included in the 1X-Z3 commercial colour and is also in the MS-41 colouring agent. Fig.12b presents a comparison of the changes in the surface concentration of chrome as a function of the ratio of laser power over the laser scanning speed for both of the decorating agents. There is a visible stabilization in the concentration of Cr for MS-41 when optimal laser firing parameters are used.

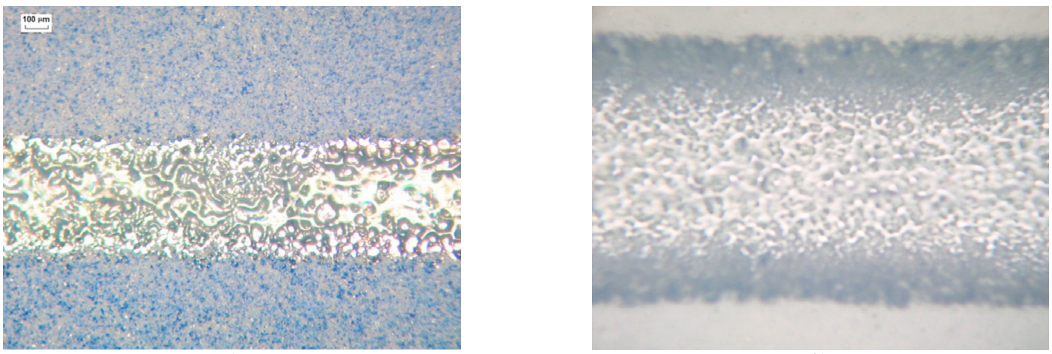



a) b)

Fig. 12. a) Results of laser illumination on a white ceramic plate with MS-41 test material (black colour) applied onto it, methodology presented in [11]; b) comparison of changes in the concentration of chrome on the glazed surface as a function of the P/v ratio for the commercial ceramic colour studied earlier, 1-XZ3 and MS-41, using optimal fusion process parameters

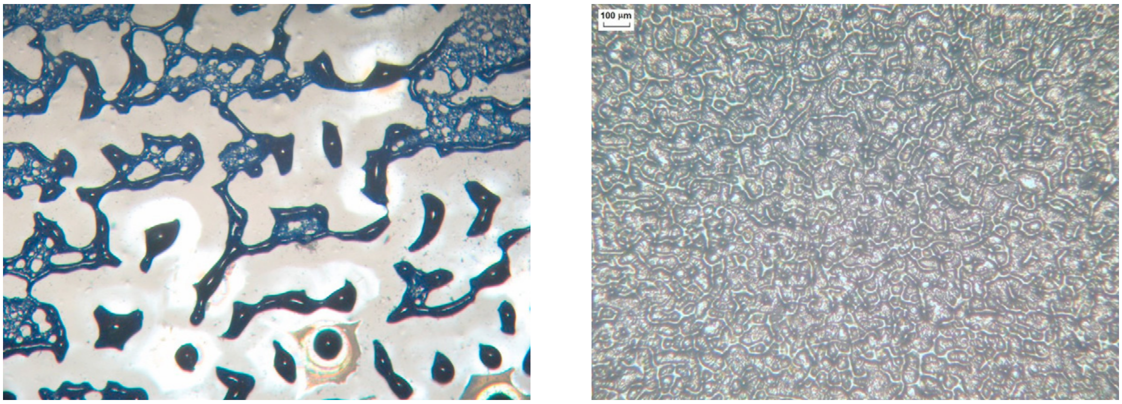
## 5. Conclusions

Profilometry studies have been conducted on sintered decorative agents that were either surfaces or lines. They show that the strength of the surface tension forces play a significant role in the formation of fired tracks and in the distribution of colouring agents on large surfaces. For high power laser beams, an additional factor affecting the distribution of the colour decorating agent is a high plasma pressure. A chemical analysis of lines fired by laser illumination was carried out. For the chrome responsible for the green hue in the 1X-Z3 colour, the movement of this element within the line was presented. This is associated with the flow of the melted colour agent and substrate material and the chemical reaction caused by the high temperature.




a) b)

Fig. 13. Comparison of the illuminated lines for different process parameters. (a) laser power 100 W, scanning speed 500 mm/s, working area placed in the focal plane; (b) laser power 100 W, scanning speed 12,5 mm/s, working area placed at a distance 10 mm from the focal plane. The width of the area in the micro-photographs is 2 mm




a) b)

Fig. 14. Comparison of the square samples illuminated with different process parameters: (a) laser power 4 W, scanning speed 5,3 mm/s; (b) laser power 50 W, scanning speed 1000 mm/s. The width of the area in the micro-photographs is 2 mm

The works conducted related to the chemical composition of the deposited material, the quality and thickness of the deposited layers and the laser treatment allowed for a significant improvement in the quality of the marked lines (Fig.13) and areas (Fig.14). Figures 13a and 14a show the results of laser exposures realized in the initial trials, using commercial ceramic colours typical for furnace firing. Test colouring agents (Fig 13b, 14b) contain additives that lower the surface tension forces and reduce the hardness of enamel.

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## References

1. Sintec Optronics Pte Ltd, Laser marking technologies. Available online: www.sintecoptronics.com/ref/LaserMarking.pdf (accessed on 18 April 2010).
2. J. F. Ready (Ed.), *LIA_handbook_of_laser_materials_processing*, Laser Institute of America, Magnolia Publishing, Inc. 2001.
3. W. M. Steen, *Laser material processing*, Springer 1991.
4. R.Akhter, L.Li, R.E.Edwards, A.W.Gale, Rapid laser surface enamelling by powder feeding technique. *App. Surf. Sci.* 208-209 (2003) 453-457.
5. F. Klocke, C. Derichs, C. Ader, A. Demmer, Investigations on laser sintering of ceramic slurries, *Prod. Eng. Res. Devel.* 1 (2007) 279–284.
6. J.W. Restrepo, J.M. Fernández-Pradas, M.A. Gómez, P. Serra, J.L. Morenza, Influence of preheating and .hematite content of clay brick pavers on the characteristics of lines marked with a Nd:YAG laser. *App. Surf. Sci.* 253 (2006) 2272–2277.
7. J.M. Fernández-Pradas, J.W. Restrepo, M.A. Gómez, P. Serra, J.L. Morenza, Laser printing of enamels on tiles*, App. Surf. Sci.* 253 (2007) 7733–7737.
8. E. Yasa, J.-P. Kruth, An Experimental study of process parameters in laser marking", in *Proc. of 5th Int. Conf. and Exhibition on Design and Production of Machines and* Dies/Molds, Kusadasi, Turkey. (2009) 213-221.
9. M. Rohde, CFD-methods applied to dispersed particie flow within melt pools during laser induced surface modification processes of ceramics, European Conference on Computational Fluid Dynamics ECCOMAS CFD 2006, P. Wesseling, E. Oñate, J. Périaux (Eds), TU Delft, The Netherlands, 2006, 1-13.
10. Institute of Ceramic and Building Materials. Offer available online: http://www.isic.waw.pl/en_zaklad_zdobniczych.php. (accessed on 7 June 2010).
11. J. Bosman, Processe and strategies for solid state Q-switch laser marking of polymers. Thesis available online: http://doc.utwente.nl/58020/1/thesis_Bosman.pdf (accessed on 18 April 2010).